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(54) SUSTAINER PROPELLANT

(71) We, AEROJET-GENERAL CORPORATION, a corporation duly organized and existing under the laws of the State of Ohio, United States of America, of 6352 North Irwindale Avenue, Azusa, State of California, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to novel solid propellant compositions and in particular to polyurethane propellant compositions of relatively low burning rate levels suitable as sustainer propellants. Sustainer propellants, as those skilled in the art realize, serve the purpose of maintaining and controlling the flight of a rocket-propelled missile to its target after the missile has been launched. The propellants used for launching missiles are known as booster propellants. Booster propellants possess high-pressure, short-duration (fast burning), high-thrust operating characteristics whereas sustainer propellants are characterized by low-pressure, long-duration (slow burning) low-thrust burning properties.

Solid propellant compositions are ordinarily composed of a resin fuel and an oxidizing material, the oxidizing material being intimately dispersed in the fuel. The ignition and burning properties of such propellant compositions, as well as their physical properties, are dependent to a large extent upon the particular resins employed as fuels as well as the particular oxidizing materials used.

It has been discovered that propellant compositions employing cross-linked polyurethanes as resin fuels and ammonium perchlorate as an oxidizing material are possessed of unexpectedly superior physical properties and performance characteristics. While these propellants, hereinafter referred to as polyurethane-ammonium perchlorate propellants, have much usefulness for many purposes, their burning rates are much too high to enable them to be used as sustainer propellants. The essence of this invention resides in our discovery of a unique propellant formulation which is essentially of the

polyurethane-ammonium perchlorate family but which differs from heretofore known polyurethane-ammonium perchlorate propellant formulations in several critical aspects. While it is essential that sustainer propellants have relatively low burning rates they should also be possessed of relatively high specific impulses. The novel propellants of this invention are unique in that their burning rates are sufficiently low to render them useful as sustainer propellants while at the same time their specific impulses are at relatively high levels.

It is thus a principal object of this invention to provide polyurethane-ammonium perchlorate propellants of sufficiently low burning rates and sufficiently high specific impulses to serve as excellent sustainer propellants.

It is another object of the invention to provide a method whereby the aforesaid propellants can be readily and practicably prepared.

The critical ingredients of our novel sustainer propellants are a polyurethane binder material, ammonium perchlorate of particle size such as to pass a 10-mesh Tyler standard screen and be retained on a 48-mesh Tyler standard screen (as an oxidizer), and a fuel which possess a high energy and a low burning rate, which fuel may be nitroguanidine, ammonium picrate, cyclonite pentaerythritoltetranitrate, mannitolhexanitrate, or nitrocellulose, or mixtures thereof. In addition, we have found it highly desirable to incorporate a burning rate depressant of a type hereinafter more fully identified into our sustainer propellants. Preferably, a plasticizer which contributes to burning rate reduction, such as trioctyl phosphate, is also incorporated into the propellant, and, in addition, various minor additives as more fully identified hereinafter can be added thereto.

Our novel sustainer propellants can be visualized as modifications of those polyurethane-ammonium perchlorate propellants previously known, of which those described in assignee's copending British Application No. 26811/60 S.N. 984960, are representative. In addition to the differences

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in critical ingredients between our unique sustainer propellants and the polyurethane propellants of British Application No. 26811/60, there is normally another significant difference there-between. Thus, our novel propellant formulations seldom contain any material which acts as a burning rate catalyst, by which is meant a catalyst to *increase* the burning rate of the propellant, whereas the incorporation of such burning rate catalysts into polyurethane-ammonium perchlorate propellants is usually common practice. The reason for the absence of burning rate catalysts in our novel propellant is, of course, obvious in view of the fact that sustainer propellants require relatively low burning rates.

In the production of composite propellants, resin fuel and oxidizer materials with various curing agents and combustion catalysts are normally blended into a slurry and then cast into a mold to form a propellant grain or cast directly into a rocket motor case to form a case-bonded grain. The case bonding procedure is preferred since by this technique it is possible to achieve higher solid propellant loading densities and to avoid the necessity of using supporting devices such as those required for the free standing grains formed by mold casting. Only solid propellants with high elongation capability can be successfully case-bonded because of the high strains induced in the case-bonded grain during changes of the environmental temperature.

Composite solid propellants of the castable type, other than polyurethane-fuel based, must be cured at high temperatures, usually 150° - 250 °F, but in some cases as high as 325°F, in order to cause completion of polymerization reactions or solvation of already polymerized binder portions. When propellant grains formed at these high temperatures are cooled to the ambient temperatures at which rockets are generally conditioned before firing, very high stresses are induced in the propellant grains causing cracks with subsequent rocket malfunction after ignition. In addition, the binder systems of these propellants show most of the polymerization after gelation which occurs after the propellants are cast; the polymerization after gelation induces stresses in the grain due to shrinkage during cure (2.5-6 percent). Rapid polymerization, 90 percent of the reaction occurring in two to twelve hours with accompanying high heat of reaction, results in high exothermic heating. This high exothermic heating is hazardous because it may result in auto-ignition of the propellant, especially in large grains. In addition, it has the deleterious effect of producing nonuniform cure of the propellant grain due to large temperature gradients. The temperature gradients are produced by the more or less adiabatic heating during the exothermic reaction and this results in nonuniform heating

of the grain causing portions of the grain to cure at different rates, thus inducing large strains and stresses above those already described as due to shrinkage due to the polymerization reactions. These problems are avoided with polyurethane-fuel based propellants as follows:

1) Absence of exothermic heating during cure for the reason that approximately 50 percent of the heat of reaction is evolved during the mixing process at which time the exothermic heating can easily be dissipated by cooling the mixer jacket, and the heat of reaction obtained in subsequent curing reactions occurs over so long a period of time (approximately three days) that no measurable heat rise is obtained during the propellant cure after casting;

2) Absence of shrinkage effects due to polymerization because the polyurethane binder does not gel until approximately 87 percent of the polymerization has been completed; since the polyurethane binder inherently has low shrinkage during cure and only 13 percent of that amount occurs after gelation, the amount of shrinkage observed in the propellant due to cure is as low as 0.06 percent; and

3) Stresses due to cooling from the curing temperature are avoided because the novel polyurethane-fuel based propellants of our invention can be cured at low temperatures, under 110°F.

Hence, for the reasons just stated, the cured grains have essentially no internal strains.

The above-described faults of composite solid propellants of the castable type other than polyurethane-fuel based ones have heretofore imposed severe restrictions upon the size of solid propellant motors containing cast-in-case case-bonded propellant grains because of the tendency of the grains toward cracking as a result of internal strains. The novel propellants of this invention are not subject to such size limitations because of the use of cross-linked polyurethanes as binder systems therein.

In addition to their freedom from cracking, the polyurethane sustainer propellants of this invention are superior in other ways. For example, they are possessed of sufficiently tenacious adhesive properties to enable them to be bonded directly to rocket chamber linings, thus permitting optimum utilization of the available rocket motor space and simplifying manufacturing techniques. Our novel polyurethane sustainer propellants are also possessed of many other desirable properties among which are rubbery mechanical qualities, low brittle point, excellent resilience, and superior aging properties.

Our novel sustainer propellants can be used as the propulsion source to sustain the flight of rocket-propelled vehicles on their path after

they have been launched by booster propellants. When thus used, our novel sustainer propellants can be conveniently ignited by a conventional igniter such as, for example, the igniter disclosed in assignee's British Patent No. 892,881. The propellant can be cast directly in the rocket chamber in which it is to be fired and restricted on one or both ends in the conventional manner with a relatively slow burning inert resin such as a polyurethane or a polyester resin. The restriction is preferably accomplished by applying a relatively thin coating of the inert resin to the inner surface of the rocket chamber lining prior to casting the propellant therein. Rocket chambers such as those in which our novel solid propellants are employed are ordinarily of the conventional type having one end open and leading into a venturi rocket nozzle. Upon ignition, large quantities of gases are produced and exhausted through the nozzle creating propulsive force.

Our novel propellant is particularly adaptable for use as the sustainer propellant in dual-thrust rocket motors of the type in which sustainer and booster propellants are disposed in abutting relationship in a common chamber or housing. In operation, the booster propellant of such a dual-thrust motor is ignited and furnishes the initial thrust to propel the rocket through the earth's atmosphere to a predetermined altitude and velocity at which point the sustainer ignites and subsequently propels the rocket motor. The ignition of the sustainer propellant is automatically accomplished by the flame from the booster when the flame front reaches the abutting sustainer grain.

The polyurethane binders of our invention are prepared by reacting a compound having two or more active hydrogen groups capable of polymerizing with an isocyanate, with an organic compound having, as the sole reacting groups, two or more isocyanate or isothiocyanate groups. The compound having the active hydrogen groups is preferably an organic compound having, as its sole reacting groups, hydroxyl, amine, substituted amine, or thiol groups.

It will be apparent that where there are more than two active hydrogen, isocyanate, or isothiocyanate groups present on any of the polyurethane reactants the resulting molecular structure of the polyurethane binder will be at least to a certain extent of a cross-linked rather than a linear nature. The cross-linking is accomplished when all three functional groups of a sufficient number of the trifunctional molecules undergo the urethane reaction with other groups present in the mixture, thus resulting in a product having a "three-dimensional" molecular structure rather than mere aggregates of linear chains as is the case when bifunctional reactants are employed.

Where bifunctional reactants such as dihydroxy compounds and diisocyanates are employed to produce the polyurethane binders for our novel propellants, it is necessary to also employ a cross-linking agent to assure a product having the cross-linked structure essential to this invention. Cross-linking agents can also be used with polyurethane reactants having more than two functional groups, such as triols and/or trisocyanates, within the scope of this invention. Compounds suitable as cross-linking agents for our polyurethane binders are those organic compounds having, as the sole reacting groups, three or more groups polymerizable with hydroxy or isocyanate groups.

It will be appreciated that in any given batch of propellant the individual polyurethane molecules may vary in number of repeating units from several to tens of thousands of these units, hence molecular weight figures on polyurethanes represent statistical averages. The exact nature of terminal groupings is not known and will vary depending upon whether plasticizers, polymerization catalysts, etc., are present. Moreover, a given molecule may even form a ring and thus leave no dangling radicals.

It is evident from the above that a wide variety of polyurethane binders for the propellants of this invention can be prepared by varying the particular isocyanate and hydroxy starting materials.

The isocyanate starting materials for our polyurethane binders are preferably diisocyanates but not necessarily so since, as explained above, other polyisocyanates (such as trisocyanates) or polyisothiocyanates may be employed within the scope of the invention if desired.

Our preferred diisocyanate compounds can be saturated or unsaturated; aliphatic or aromatic; open or closed chain, and, if the latter, monocyclic or polycyclic; and substituted or not by groups substantially unreactive with isocyanate or hydroxyl groups such as, for example, ketone, halogen, ester, sulfide, or ether groups. The following diisocyanate compounds are particularly suitable as reactants for the preparation of binders for our novel polyurethane propellants:

- (a) Alkane diisocyanates such as:
  - ethylene diisocyanate;
  - trimethylene diisocyanate;
  - propylene-1,2-diisocyanate;
  - tetramethylene diisocyanate;
  - butylene-1,3-diisocyanate;
  - decamethylene diisocyanate;
  - octadecamethylene diisocyanate;
- (b) Alkene diisocyanates such as:
  - 1-propylene-1,2-diisocyanate;
  - 2-propylene-1,2-diisocyanate;
  - 1-butylene-1,2-diisocyanate;
  - 3-butylene-1,2-diisocyanate;
  - 1-butylene-1,3-diisocyanate;

1	butylene-2,3-diisocyanate;	cyclohexylene-1,3-diol;	
	(c) Alkylidene diisocyanates such as:	cyclohexylene-1,4-diol;	
	ethylidene diisocyanate;	(4) Aromatic diols such as:	
5	propylidene-1,1-diisocyanate;	catechol;	70
	propylidene-2,2-diisocyanate;	resorcinol;	
	(d) Cycloalkylene diisocyanates such as:	quinol;	
	cyclopentylene-1,3-diisocyanate;	1-methyl-2,4-benzenediol;	
	cyclohexylene-1,2-diisocyanate;	2-methyl-1,3-naphthalenediol;	
10	cyclohexylene-1,3-diisocyanate;	2,4-toluenediol;	75
	cyclohexylene-1,4-diisocyanate;	(5) Aliphatic-aromatic diols such as:	
	(e) Cycloalkylidene diisocyanates such as:	xylylene-1,4-diol;	
	cyclopentylidene diisocyanate;	xylylene-1,3-diol;	
	cyclohexylidene diisocyanate;	1,5-naphthalene dimethanol;	
15	(f) Aromatic diisocyanates such as:	2-ethyl-1-phenyl-3-butene-1, 2-diol;	80
	<i>m</i> -phenylene diisocyanate;	2,2-di-(4-hydroxyphenyl) propane;	
	<i>o</i> -phenylene diisocyanate;	(6) Diols containing hetero-atoms such as:	
	<i>p</i> -phenylene diisocyanate;	di-( <i>B</i> -hydroxyethyl) ether;	
	1-methyl-2,4-phenylene diisocyanate;	6-methyl-2,4-pyrimidinediol;	
20	naphthylene-1,4-diisocyanate;	$\text{HOCH}_2\text{CNH}(\text{CH}_2)_6\text{NHCCH}_2\text{OH}$ .	85
	2,4-tolylene diisocyanate;		
	2,6-tolylene diisocyanate;	Other dihydroxy compounds suitable for the	
	4,4'-diphenylmethane diisocyanate;	polyurethane reaction of this invention are	
	1,5-naphthalene diisocyanate;	polyesters such as those obtained from the	
	methylene- <i>bis</i> -(4-phenylisocyanate);	reaction of a dihydric alcohol such as ethylene	
25	2,2-propylene- <i>bis</i> -(4-phenylisocyanate);	glycol, diethylene glycol, propylene glycol,	90
	diphenylene-4-4'-diisocyanate;	butylene glycol, or hexamethylene glycol with	
	(g) Aliphatic-aromatic diisocyanates such	a dicarboxylic acid such as succinic acid, adipic	
	as:	acid, sebacic acid, oxadibutyric acid, or	
30	xylylene-1,4-diisocyanate;	sulfodipropionic acid. The polyesters most	
	xylylene-1,3-diisocyanate;	suitable for purposes of this invention are	95
	4,4'-diphenylenemethane diisocyanate;	those having a molecular weight from about	
	4,4'-diphenylenenepropane diisocyanate;	1000 to about 2500. In preparing polyesters	
	(h) Diisocyanates containing hetero-atoms	such as these, the dihydric component is	
35	such as:	permitted to react with the dicarboxylic acid	
	$\text{OCN-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-NCO}$ :	component to produce the polyester. Mixtures	100
	2,3-pyridine diisocyanate.	of polyesters and an olefin such as styrene, or	
	The preferred hydroxy starting materials for	vinyl acetate, are particularly suitable for	
	our polyurethane binders are dihydroxy	purposes of this invention. The olefin does not	
40	compounds having the general formula	react with any of the hydroxy groups present	
	$\text{HO-R-OH}$ ; where R is a divalent organic	in the mixture nor does it interfere in any way	105
	radical. The hydroxy groups on the above	with the subsequent reaction between these	
	compounds can be of any type suitable for the	hydroxyl groups and the isocyanate groups in	
45	urethane reaction with isocyanate groups such	the polyurethane reaction mixture. Neither	
	as, for example, alcohol or phenolic hydroxy	does it interfere with any reactions of cross-	110
	groups. The following dihydroxy compounds	linking agents present in the mixture. The	
	are particularly suitable as reactants for the	principal function of the olefin is to permit	
	polyurethane binders of this invention:	linkage of the polyester molecules together	
	(1) Alkane diols having a chain length of	through addition polymerization.	
50	from 2 to 20 carbon atoms, inclusive, such as:	The above-mentioned polyesters can be	
	2,2-dimethyl-1,3-propanediol;	prepared from either saturated or unsaturated	115
	ethylene glycol;	dihydric alcohols and saturated or	
	tetramethylene glycol;	unsaturated dicarboxylic acids. The anhydrides	
	hexamethylene glycol;	of any of the dicarboxylic acids can be	
55	octamethylene glycol;	substituted for all or part of any of them in the	
	decamethylene glycol;	preparation of polyesters suitable for the	120
	(2) Alkene diols such as:	polyurethane reaction of our invention. The	
	1-propylene-1,2-diol;	usual and preferred manner of making	
	2-propylene-1,3-diol;	suitable polyesters is to react a mixture of a	
60	1-butylene-1,2-diol;	saturated dicarboxylic acid (such as adipic acid	
	3-butylene-1,2-diol;	or sebacic acid or anhydride and an unsaturated	125
	1-hexylene-1,3-diol;	or aromatic dicarboxylic acid or anhydride	
	1-butylene-2,5-diol;	with a dihydric alcohol. Examples of	
	(3) Cycloalkylene diols such as:	unsaturated dicarboxylic acids which can be	
65	Cyclopentylene-1,3-diol;	employed are: maleic acid, fumaric acid,	
	cyclohexylene-1,2-diol;	citraconic acid, mesaconic acid and itaconic	130

acid.

In addition to the polyesters, polyethers such as polyethylene ether glycols, polypropylene ether glycols, other polyalkylene ether glycols, and mixtures or copolymers thereof, having molecular weights of from about 400 to about 10,000 can be utilized as dihydroxy reactants of the polyurethane reaction of this invention. The preferred polyethers of this invention are the polypropylene glycols having a molecular weight of from 2,000 to 3,000.

Polysulfides having two or more thiol groups, such as ethylene disulfide and the Thiokols ("Thiokol" is a registered Trade Mark) produced by Thiokol corporation, and polysulfides with glycol end groups such as those having the general formula  $\text{HO}(\text{CH}_2\text{CH}_2\text{S-S})_x\text{CH}_2\text{CH}_2\text{OH}$ , where  $x$  is a whole number, are other suitable reactants for the polyurethane reaction of our invention.

It will be appreciated by those skilled in the art that mixtures of suitable polyhydroxy and/or polyisocyanate compounds can be used for purposes of this invention if desired.

It is well-known to those skilled in the art that polyisothiocyanates and polythiol compounds react to yield urethane-type products as do the polyisocyanates and polyol compounds. Consequently, the polyisothiocyanates and polythiols and corresponding to any of the polyisocyanates or polyhydroxy compounds taught herein can be employed for the preparation of propellant binders useful in this invention. For example, diisothiocyanates such as butylene-1,3-diisothiocyanate; ethylidene diisothiocyanate; cyclohexylene-1, 2-diisothiocyanate; cyclohexylidene diisothiocyanate; *p*-phenylene diisothiocyanate; and xylylene-1,4-diisothiocyanate; react with dithiol compounds such as decamethylene dithiol; thioresorcinol; ethylene-*bis*-(thioglycolate); to yield polythiourethane compounds which are suitable as binders for our novel propellant compositions. Any mixture of the diisocyanates and/or diisothiocyanates suitable as reactants for the propellant binders of this invention can be reacted with any mixture of diols and/or dithiols disclosed as suitable for the purpose within the scope of our invention.

It will be appreciated by those skilled in the art that a great variety and number of polyfunctional organic compounds will serve as cross-linking agents for the polyurethane binders of this invention. As indicated above, any organic compound having as its sole reacting groups three or more groups polymerizable with hydroxy or isocyanate groups is a suitable cross-linking agent for purposes of this invention. This includes not only the obvious polyfunctional hydroxy,

thiol, isocyanate, and isothiocyanate compounds but also compounds containing other groups polymerizable with either hydroxy or isocyanate groups. For example, compounds with three or more groups containing reactive hydrogen which are capable of polymerization with isocyanates can be employed as cross-linking agents within the scope of this invention. Examples of compounds of this class are proteins and synthetic polyamides such as polyhexamethylene adipamides. The cross-linking agents of this invention can be saturated or unsaturated; aliphatic or aromatic; open or closed chain, and, if the latter, monocyclic or polycyclic; and substituted or not by groups substantially unreactive with isocyanate or hydroxyl groups such as, for example, ketone, halogen, ester, sulfide, or ether groups.

Examples of compounds which we have found to be particularly suitable as cross-linking agents are glyceryl monoricinoleate; glyceryl triricinoleate (referred to hereinafter as GTRIO); 1,2,6-hexanetriol; methylene *bis*-(orthochloroaniline); monohydroxyethyl trihydroxypropyl ethylenediamine; polyaryl polyisocyanates; pentaerythritol-propylene oxide adduct; N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine; triethanolamine; trimethylolpropane; triisocyanates such as 2,4,6-tolylene triisocyanate; and adducts of polyols and diisocyanates such as the reaction product of glyceryl monoricinoleate with less than one-half the reaction equivalence of tolylene diisocyanate.

Other substances suitable as cross-linking agents are glycerol, sorbitol, dextrin, starch, cellulose, polyvinyl alcohol, diethylenetriamine, polyvinyl mercaptans, and shellac.

As in the case of the polyurethane reactants, mixtures of the various cross-linking agents can be employed within the scope of this invention.

The selection of a suitable oxidizing salt for a solid propellant grain is normally a simple matter involving merely the selection of an oxidizer exhibiting burning properties of the type desired in the grain. In view of this there would appear to be no particular difficulty in the preparation of a low burning rate polyurethane sustainer propellant by simply choosing ammonium nitrate, which is known to exhibit a relatively low burning rate, as the oxidizer. However, it has been found that ammonium nitrate is somewhat undesirable for use with polyurethane binders in that it tends to cause degradation of the polyurethane polymers and to bring about instability thereof under storage at elevated temperatures.

The novel method of our invention comprises a means of furnishing excellent polyurethane-fuel based sustainer propellants without resorting to the use of ammonium

nitrate as an oxidizer. This is accomplished by employing coarse ammonium perchlorate as an oxidizer in conjunction with various special ingredients to tailor the burning rate of the finished grain to the desired sustainer propellant level. Our novel sustainer propellants are limited to the use of ammonium perchlorate as an oxidizer because it yields the highest specific impulse of any available oxidizing salt in its coarse form, it results in a desirably slow burning rate, and it is completely compatible with polyurethane binders. No other known oxidizer is possessed of these particular properties and characteristics, all of which are essential to the preparation of a satisfactory polyurethane sustainer propellant.

It is important that at least part of the ammonium perchlorate in our novel sustainer propellants be of coarse particle size since oxidizer particle size is a critical variable in achieving the desired propellant burning rate, fine ammonium perchlorate having been found to result in an undesirably high burning rate. Preferably, the ammonium perchlorate for use in our sustainer propellants should be of such particle size as to pass a 10-mesh Tyler standard screen and be retained on a 48-mesh Tyler screen.

In the preparation of booster propellants it is customary to employ a blend of coarse and fine oxidizer material in order to achieve optimum castability in the propellant mix. However, we have discovered that good castability can be achieved in our sustainer propellant mixes without resorting to fine particle-size oxidizer since the nitroguanidine has been found to serve the same purpose as finely divided oxidizer in this respect. While it is true, as stated above, that it is not necessary to employ coarse-fine blends of oxidizer in our novel sustainer propellants, such mixtures can, of course, still be used within the scope of this invention and, in fact, we have found it desirable in most cases to utilize some finely ground oxidizer along with the coarse material.

As indicated above, it is essential that our novel sustainer propellants contain a fuel material since in the absence of such material they would exhibit inordinately high burning rates for sustainer utility (although they would be useful as booster propellants). Examples of such fuels are nitroguanidine, ammonium picrate, and mixtures thereof. Other high energy, low burning rate fuels which can be utilized within the scope of this invention are cyclonite, pentaerythritol, tetranitrate, manitol, hexanitrate, and nitrocellulose. Nitroguanidine is our preferred low burning rate fuel because of its ready availability, low cost, good compatibility, freedom from objectionable side reactions, good mixing characteristics, and low detonation susceptibility; and the fact that greater burning rate reduction per percent

incorporated can be attained, that reduction of specific impulse is minimized, that lower flame temperatures can be obtained, and that aging characteristics of propellants are not impaired.

While not an essential ingredient of our novel propellant compositions, a burning rate depressant is normally incorporated therein in addition to the low burning rate fuel. Materials which we have found to be useful as burning rate depressants are normally substances which decompose endothermally although substantially inert high melting materials such as zirconium silicate, silica, and alumina, absorb heat, particularly when melting, and, as a result, also function as burning rate depressants.

Representative of the endothermally decomposable materials suitable as burning rate depressants are salts of metals having only one valence state such as the alkali and alkaline earth metal phosphates, oxalates, carbonates, carbamates and borates. Other suitable burning rate depressants are the endothermally decomposable ammonium salts such as the phosphates, oxalates, carbonates, carbamates and borates. It is felt that the burning rate depressants slow down the burning rate of a propellant by lowering the flame temperature through the absorption of heat.

Examples of materials which are suitable as burning rate depressants are polyvinyl chloride resins, oxamide, calcium oxalate, calcium carbonate, calcium fluoride, calcium phosphate, nickel fluoride, nickel carbonate, nickel phosphate, zirconium silicate, lithium carbonate, diammonium phosphate, magnesium phosphate, sodium tetraborate, calcium metaborate, magnesium metaborate, ammonium phosphomolybdate, and complexes of ammonium silicomolybdate such as the triethanolamine complex thereof. The preferred type of polyvinyl chloride resin is the low molecular weight, low fusion temperature type used for adhesives, as exemplified by that known commercially as GEON 428. Another example of a polyvinyl chloride resin suitable for purposes of this invention is available under the trade name GEON 222 ("GEON" is a registered Trade Mark).

The following advantages accrue from the use of polyvinyl chloride resins in sustainer propellants:

1) The material is a burning rate depressant which does not result in deterioration of age life and mechanical properties of propellants and

2) It is a pressure exponent depressant such that the slope can thereby be reduced from approximately 0.25 to approximately  $0.00 \pm .05$  in the operating pressure range of sustainer propellants (200-400 psia).

Calcium oxalate is our preferred nonresin

depressant because of its degree of depressant effect, its lack of effect upon polymer degradation, its availability, its cost, its lack of toxicity, its depression of the ignition of the propellant, its effectiveness at low concentrations, and its even dispersal when mixed into the propellant. Mixtures of burning rate depressants such as those named above can be used within the scope of our invention if desired.

In the preparation of solid propellants, plasticizers familiar to those skilled in the art such as isodecyl pelargonate; 4-nitrazapentanitrile; 2,2-dinitropropyl-4-4-nitrazapentanoate; di-(2-ethyl-hexyl) azelate; as well as those commercially available as such; are normally utilized. Where polyurethane binders are used, the preferred plasticizer is normally di-(2-ethylhexyl) azelate or isodecyl pelargonate.

While conventional polyurethane plasticizers, such as those mentioned above, can be used in our novel propellants, we have found that their use usually results in some increase in propellant burning rate which is, of course, undesirable in sustainer propellants. Consequently, we have found it preferable to employ as a plasticizer a material which achieves a reduction in burning rate below that attainable with conventional plasticizers. Examples of materials which accomplish such a purpose are phosphate and borate esters such as, for example, trioctyl phosphate, tricresyl phosphate and octylphenyl phosphate. Trioctyl phosphate is our preferred plasticizer because it provides a 10-20 percent reduction in burning rate by comparison with conventional plasticizers such as di-(2-ethyl-hexyl) azelate and isodecyl pelargonate; it possesses good compatibility with polyurethanes; it contributes to improved safety characteristics of the propellant; and it has the lowest brittle point of the known depressant plasticizers, resulting in the most desirable low temperature mechanical properties in the finished propellant.

In addition to the ingredients described above, various other additives can be employed in preparing the sustainer propellants of this invention. For example, catalysts for the polyurethane reaction such as triethylamine and other tertiary amines; ferric acetylacetonate and other metal acetylacetonates such as vanadyl acetylacetonate; stannic chloride; organo tin compounds such as dibutyl tin oxide; can be employed if desired. The catalysts can be employed in quantities within the range from mere traces up to amounts equivalent to about 1 percent by weight of the total mass and even higher. Normally, amounts of from about 0.02 to about 0.10 percent by weight, on a total weight basis, are employed.

The polymerization reaction may be carried out either in a suitable solvent or in the

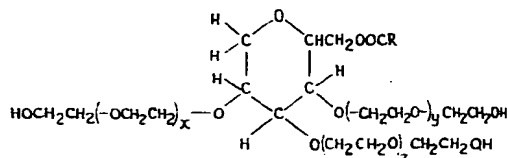
absence of a solvent. The solvent may be present in such great excess as to form a solution of monomers or may be used in relatively small quantities. Suitable solvents are those in which the various ingredients of the reactant mixture are soluble such as 4-nitrazapentanoate, dioxane and dimethylphthalate.

Other additives such as antioxidants, wetting agents and anti-foaming agents, can be employed if desired in the formulation of our novel propellants. For example, in order to overcome porosity due to gasification in our novel propellant formulations, a silicone oil may be added as an antifoaming agent to the propellant mix. The use of silicone oils as antifoaming agents in our propellant mixes results in improved processing, reduces foaming of the propellant ingredients during mixing, aids in vacuumization of the mix, and reduces porosity in the cured propellants. A preferred silicone oil antifoaming agent is polydimethylsiloxane of approximately 1000 cstks viscosity at 25°C such as that available commercially under the trade name LINDE L-45. Antifoaming agents are added to the propellant mix in small quantities, normally in an amount not greater than about 0.01 percent by weight of the mix.

We have found certain well-known wetting agents such as lecithin to be useful processing aids in the preparation of our novel propellants. A wetting agent which we have found to be particularly suitable for our purpose is that known commercially as G-2684, a mixture of sorbitan monooleate and polyoxyethylene esters of mixed fatty and resin acids. Other wetting agents useful for our purpose are materials having the general formula



wherein R is an aliphatic 17 to 24 carbon group and R<sub>1</sub> is a polypropylene oxide group. An example of this type of agent is that known commercially as Priminox-10. Still other suitable wetting agents for use in our novel propellants are sorbitan trioleate and the polyoxyethylene sorbitan monooleates having the general formula



wherein R is a fatty acid residue and x, y, and z are positive whole numbers which can be the same or different.

A product representative of the latter class of materials is available on the commercial market under the trade name Tween 21 ("Tween" is a registered Trade Mark). As is well-known to those skilled in the art, wetting

agents, or as they are sometimes called, surface active agents, are useful in improving the processibility and castability of solid propellant mixes. For best results we have determined that wetting agents should be incorporated into our novel propellant formulations in proportions not greater than about 1 percent by weight, on a total weight basis, and preferably in amounts substantially lower than this.

It is within the scope of our invention to employ mixtures of wetting agents in our propellant formulations. We have found a mixture of lecithin, Priminox-10, and sorbitan trioleate to be a synergistic wetting agent system which provides maximum castability in the presence of nitroguanidine. The Priminox-10 and sorbitan trioleate are polymeric and result in better mechanical properties for propellants. Priminox-10 also acts as a cure promoter. A multifunctional wetting agent system results in additional advantages in cure and physical properties of final propellant.

In addition to the above-mentioned additives there are numerous others which can be employed in minor amounts within the scope of our invention. For example, as indicated above, materials useful as antioxidants can be utilized in the propellants of this invention and one such material which we have found to be particularly suitable for that purpose is N,N'-diphenyl-p-phenylenediamine.

In addition to those additives which are added in minor amounts to our novel propellants there are other noncritical ingredients which can be employed within the scope of this invention. For example, it is within the scope of the invention to incorporate finely divided aluminum in amounts up to about 22 percent by weight into the propellants, the preferred quantity being in the neighborhood of about 10 percent by weight, on a total propellant weight basis. When quantities greater than about 22 percent are used, serious combustion difficulties are normally encountered.

The aluminum improves the tensile properties of propellants by acting as a reinforcing constituent in a manner somewhat analogous to the action of aluminum powder as a filler in adhesives to improve the strength of the glue line. In addition, the aluminum powder occupies a smaller volume than other propellant ingredients, providing more fuel between particles. The use of aluminum also permits a lower oxidizer concentration which results in a higher fuel content. Increasing fuel content yields higher values of elongation at low temperatures resulting in less tendency to crack or fail during cycling.

We have determined that the use of aluminum powder as an ingredient of our sustainer propellants results in a lowering of burning rate below that otherwise obtainable

and good castability properties. Relatively high specific impulses in the order of 200 lb-sec/lb at 230 psia are available through such use of aluminum as an ingredient of our sustainer propellants. The increase in specific impulse is caused by the additional energy obtained from the combustion of aluminum, and the increased hydrogen content in the gas stream resulting from the strong affinity of aluminum with oxygen from the propellant ingredients. Examples of aluminum powders suitable for our purpose commercially available are Alcoa grade 120, having an average particle size of 76  $\mu$ , Reynolds grade 1-511, having an average particle size of 40  $\mu$ , and Reynolds grade 400, having an average particle size of 7  $\mu$ . ("Alcoa" and "Reynolds" are registered Trade Marks.)

In preparing the novel propellants of this invention, the polyurethane polymerization can be conducted at any temperature, the only effect of temperature variation being a corresponding increase or decrease in the rate of reaction. The polymerization readily takes place at room temperature but higher temperatures increase the rate of reaction and are therefore desirable in many cases. As explained above, however, temperatures lower than as well as higher than room temperature can be used for our polymerization reaction.

Because higher temperatures tend to produce shrinkage and internal strains, it is preferable to carry out the cure at temperatures in the range of from about 70° to about 180°F. Within this range the reaction rate is sufficiently rapid for economical production and yet the temperature is not so high as to produce shrinkage and internal stresses which must be avoided at all costs, especially in the case of large solid propellant motors.

Those skilled in the art will appreciate the fact that heating and cooling steps can be incorporated into our propellant processing procedure for various reasons, such as for the attainment of optimum operating conditions, if desired. Likewise, various other techniques which serve to optimize the processing procedure or improve the quality of the product (such as vacuumizing the mixture during certain phases of the operation) can be employed in the practice of this invention if desired.

The various processing steps of this invention can be carried out with standard equipment well-known to those skilled in the art as suitable for the purpose. A mixer which we have found to be particularly effective for mixing our propellant ingredients, however, is that known commercially as the BP mixer. The BP mixer is manufactured by Baker-Perkins, Inc., of Saginaw, Michigan, and it can be equipped with facilities for heating, cooling, and vacuumizing propellant batches during mixing for use where such facilities



appear to be warranted.

After the propellant batch has been mixed to substantial uniformity, it is cast, extruded, or compression-formed to the desired shape and cured at a temperature preferably within the range from about 70° to about 180°F. As pointed out above, the propellant mixture can be cast directly into a rocket chamber lined with an inert material and polymerized (cured) therein if this procedure appears to be desirable.

From about 50 to 80 weight percent of ammonium perchlorate is preferably employed in the preparation of our novel solid propellants. The amount of binder used should, for best results, be within the range from about 55 to about 5 percent (the preferred range being from about 15 to about 30 percent) by weight of the final propellant. The term binder, as used herein, refers to the polyurethane constituent (including the cross-linker of our propellants. We have found the operative proportions of high energy, low burning rate fuel (such as nitroguanidine for use in the propellants of this invention to be those from about 5 to about 40 percent by weight, with the preferred proportions not exceeding about 25 percent, all proportions being given on a total propellant weight basis.

The burning rate depressant of this invention, such as calcium oxalate, should be employed in quantity within the range from about 1 to about 8 percent by weight for best results, the preferred quantity being about 3 percent, all percentages being given on a total propellant weight basis. Where trioctyl phosphate or its equivalent is utilized as a low burning rate plasticizer in our novel sustainer propellants, it is added in an amount within the range from about 10 to about 25 percent, and preferably in the neighborhood of about 20 percent, by weight of the final propellant grain.

The proportions of the ingredients which go to make up the binder can vary through wide ranges depending on the properties desired in the propellant and the specific reactants employed.

Although stoichiometric proportions of hydroxy and isocyanate components can be employed in the preparation of the polyurethane binders of our novel solid propellants, we have found that a product of improved mechanical properties is obtained if a slight excess of isocyanate groups over hydroxy groups is present in the binder mixture. Consequently, for best results we

have found that there should be from about 100 to about 115 equivalents of isocyanate or isothiocyanate containing monomer in the fuel mixture for every 100 equivalents of hydroxy or thiol containing monomer therein.

There can, of course, be more than one isocyanate compound or equivalent, as well as more than one hydroxy compound or equivalent, in the fuel mixture, in which case the calculation of excess isocyanate over hydroxy groups is based upon the total amounts of all pertinent compounds present. For example, where the cross-linker is a polyhydroxy compound the excess of isocyanate compound (or equivalent) is calculated as an excess over the amount of diol (or its equivalent) plus the amount of cross-linker. The relative proportions of diol and cross-linker can vary through wide ranges so long as a cross-linked structure in the fuel results therefrom.

There are many ways of processing the various ingredients within the scope of this invention in the formulation of our novel sustainer propellants. For example, where the polyurethane reactants are diols and diisocyanates and the cross-linkers are polyhydroxy compounds, the diol can be first mixed with the cross-linker after which the inorganic oxidizer, the diisocyanate, and the low burning rate fuel can be stirred or otherwise mixed into the mass. The various other additives can be introduced into the mixture prior to, at the same time as, or subsequent to the addition of the diisocyanate. The various additives are not necessarily added at the same stage of processing and, in fact, it has been found preferable in most cases to deviate from this procedure, at least to some extent. The minor components of our novel sustainer propellants, such as the antioxidants, catalysts, wetting agents, and antifoaming agents, normally comprise a relatively small percentage of the total propellant weight, usually being present in combined amount not greater than that corresponding to about 10 percent (and preferably 4 or 5 percent) of the total propellant weight.

Following are examples included for purposes of illustrating the novel process and propellant compositions of this invention. It is emphasized that these examples are intended for illustrative purposes only and that they should not be construed as limitative of the scope of the invention to the particular conditions and embodiments set forth therein.

## EXAMPLE I

This example describes the preparation of a sustainer propellant according to this invention in which a mixture of nitroguanidine and ammonium picrate is employed as the low burning rate fuel constituent. The formulation of the propellant is given below:

	INGREDIENT	WEIGHT PERCENT
10	Ammonium perchlorate - 10 to 48 mesh	31.00
	Ammonium perchlorate - fine grind	16.00
	Nitroguanidine	7.50
	Ammonium picrate	23.50
15	N,N'-diphenyl-p-phenylenediamine	0.25
	Calcium oxalate (anhydrous powder)	2.00
	Lecithin	0.09
	G-2684 wetting agent	0.06
	Polydimethylsiloxane (1000 cstks)	0.01
	Ferric acetylacetonate	0.10
20	Trioctyl phosphate	3.91
	Glyceryl monoricinoleate (GMRO)	2.07
	Polypropylene glycol 2025 * (PPG)	11.18
	2,4-Tolylene diisocyanate (TDI)	2.33
25		100.00

Equivalent percent ratio of monomers

PPG/GMRO/TDI of 50/50/110

\*Manufacturer's designation indicating the value of the molecular weight.

The following ingredients were charged to a suitable stainless steel kettle equipped with a heating jacket, agitator, source of heat, vacuum, sight glasses, safety release, draw-off valve, and utility connections:

polypropylene glycol  
glyceryl monoricinoleate  
trioctyl phosphate  
polydimethylsiloxane  
lecithin  
G-2684  
calcium oxalate

These materials were well mixed and the ammonium picrate added slowly under agitation. As soon as all of the picrate was wetted, the kettle was vacuumized to at least 29 in. vacuum. The heating, agitation, and vacuumization was continued until a temperature of 180°F was reached under full vacuum. The dehydration was continued at 180°F until the water content was less than 0.08 percent.

The hot premix was transferred to a double sigma blade mixer equipped with a heating and cooling jacket and suitable controls, utilities, and lid. Hot oxidizer (180°F) was then added by increments. The N,N'-diphenyl-p-phenylenediamine was next added and mixed in. Nitroguanidine was added directly to the mixer in two or three increments with mixing. Care was exercised to see that the amount of nitroguanidine added at a time was not excessive and that it mixed in very quickly. As soon as all of the nitroguanidine was

incorporated the mixer was closed and vacuumized slowly with blades turning until full vacuum was reached. Temperature was maintained at 120°F or higher and vacuum was brought to 29 in. Hg and held for 40 minutes with mixing and heating as necessary.

The propellant mix was cooled to 68°F so that the entire mix was at this temperature. Two-thirds of the 2,4-tolylene diisocyanate was added slowly through an addition device to the mixer. The entire mix was mixed and vacuumized at 66-68°F for one hour. The balance of the 2,4-tolylene diisocyanate containing ferric acetylacetonate was added and mixed with cooling and vacuumization for 20 minutes. The propellant was then cast.

The mixing operation was carried out under humidity controlled conditions (20 percent humidity). All sources of water were excluded from the propellant. Dried additives were used. Vacuum was broken with dry N<sub>2</sub>.

Premix dehydration was carried out to remove water safely from ammonium picrate. Hot oxidizer and propellant mix heating were for the purpose of removing all traces of moisture and volatiles. Mix was cooled to 68°F before addition of the 2,4-tolylene diisocyanate to prevent polymerization and reduction of castability. Addition of two-thirds of the 2,4-tolylene diisocyanate without catalyst followed by vacuumization resulted in the formation and pulling off of objectionable reaction products which promote porosity.

The propellant was cured initially for 24 hours at 70°F to reduce objectionable reactions and reduce porosity and then subjected to a further cure of 48 hours at 110°F.

## EXAMPLE II

This example describes the preparation of a sustainer propellant according to this invention in which nitroguanidine was employed as the low burning rate fuel ingredient. The formulation of this example is given below:

	INGREDIENT	WEIGHT PERCENT
	Ammonium perchlorate - 10 to 48 mesh	53.20
	Ammonium perchlorate - fine grind	7.80
	N,N'-diphenyl-p-phenylenediamine	0.25
	Calcium oxalate	2.00
	Lecithin	0.25
	G-2684	0.06
	Ferric acetylacetonate	0.10
	Trioctyl phosphate	3.87
	Polypropylene glycol 2025	11.12
	Glyceryl monoricinoleate	2.05
	2,4-Tolylene diisocyanate	2.30
	Nitroguanidine	17.00
		100.00

The premix was made of all liquid ingredients except 2,4-tolylene diisocyanate by weighing out each of the ingredients and adding same to a dry, clean, stainless steel pot equipped with

agitation and a drain-off valve. The liquid ingredients were polypropylene glycol, glyceryl monoricinoleate, trioctyl phosphate, polydimethylsiloxane, sorbitan trioleate, Priminox 10, and lecithin. The premix was transferred to a double sigma blade mixer. The hot oxidizer was then added from the transfer bin through a feeding device to the operating mixer. Flow of oxidizer was controlled so that it was mixed in as fast as added. As soon as all the oxidizer was added and mixed in, the other dry ingredients added one at a time. They were N,N'-diphenyl-*p*-phenylenediamine, burning rate depressant (calcium oxalate), and ferric acetylacetonate. Prescreened nitroguanidine had been weighed out into drums in six equal portions. The nitroguanidine was added to the static mix directly, a portion at a time. The nitroguanidine was spread evenly over the ingredients in the mixer and the lid lowered but not fastened down and the mixer started and operated for about five minutes to mix in the dry powder. The mixer was shut off and another portion of nitroguanidine added, etc. The mix was quite viscous at this point.

The mixer was closed and about 5-10 in. Hg vacuum applied with the mixer shut off. The mixer was started and the temperature of the mix maintained at 120°F. The mixer was operated and vacuum slowly increased until full vacuum was reached. It was necessary to apply vacuum slowly since a large amount of air had been occluded in the bulky nitroguanidine and rapid vacuumization would cause the level of the mix to rise rapidly and plug the vacuum line. The mixing at 120°F was carried on for about 45 minutes after full vacuum had been reached. The mix gradually became more fluid and the level in the mixer dropped.

The propellant was cooled with mixing and vacuumization to a temperature of 68°F. Care was exercised to make sure that all portions of the mix were at least down to 68°F or lower. 2,4-Tolylene diisocyanate was added slowly to the mixer by means of a special addition device while mixing under vacuum. The mixing was continued for 20 minutes after the 2,4-tolylene diisocyanate addition had been completed. Propellant was then cast into motors and cured for 24 hours at 70°F plus 48 hours at 110°F.

Following are other propellant formulations from which propellant grains were prepared according to methods similar to those described in Examples I and II

## EXAMPLE III

INGREDIENT	WEIGHT PERCENT	
Ammonium perchlorate - 10 to 48 mesh	53.20	70
Ammonium perchlorate - fine grind	7.80	
N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	
Calcium oxalate	2.00	
Lecithin	0.20	
Sorbitan trioleate	0.20	75
Polydimethylsiloxane (1000 cstks)	0.01	
Ferric acetylacetonate	0.10	
Trioctyl phosphate	3.85	
Polypropylene glycol 2025	11.06	
Glyceryl monoricinoleate	2.04	80
2,4-Tolylene diisocyanate	2.29	
Nitroguanidine	17.00	
	100.00	

## EXAMPLE IV

INGREDIENT	WEIGHT PERCENT	
Ammonium perchlorate - 10 to 48 mesh	53.20	
Ammonium perchlorate - fine grind	7.55	90
N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	
Calcium oxalate	2.00	
Lecithin	0.20	
G-2684	0.03	
Sorbitan trioleate	0.17	95
Polydimethylsiloxane (1000 cstks)	0.01	
Ferric acetylacetonate	0.10	
Trioctyl phosphate	4.30	
Polypropylene glycol 2025	12.35	
Glyceryl monoricinoleate	2.28	100
2,4-Tolylene diisocyanate	2.56	
Nitroguanidine	15.00	
	100.00	

## EXAMPLE V

INGREDIENT	WEIGHT PERCENT	
Ammonium perchlorate - 10 to 48 mesh	53.20	
Ammonium perchlorate - fine grind	7.80	110
N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	
Calcium oxalate	2.00	
Lithium carbonate	1.00	
Priminox 10	0.20	
Sorbitan trioleate	0.20	115
Polydimethylsiloxane (1000 cstks)	0.01	
Ferric acetylacetonate	0.10	
Trioctyl phosphate	4.05	
Polypropylene glycol 2025	11.65	
Glyceryl monoricinoleate	2.14	120
2,4-Tolylene diisocyanate	2.40	
Nitroguanidine	15.00	
	100.00	

60 125

65 130

## EXAMPLE VI

	<u>INGREDIENT</u>	<u>WEIGHT PERCENT</u>
5	Ammonium perchlorate – 10 to 48 mesh	53.20
	Ammonium perchlorate – fine grind	7.80
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25
	Calcium oxalate	2.00
	Lithium carbonate	1.00
10	Lecithin	0.10
	Priminox 10	0.10
	Sorbitan trioleate	0.20
	Polydimethylsiloxane (1000 cstks)	0.01
	Ferric acetylacetonate	0.10
15	Trioctyl phosphate	4.05
	Polypropylene glycol 2025	11.65
	Glyceryl monoricinoleate	2.14
	2,4-Tolylene diisocyanate	2.40
	Nitroguanidine	15.00
20		100.00

## EXAMPLE IX

	<u>INGREDIENT</u>	<u>WEIGHT PERCENT</u>	
	Ammonium perchlorate – 10 to 48 mesh	53.20	70
	Ammonium perchlorate – fine grind	7.80	
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	
	Lecithin	0.10	
	Priminox 10	0.10	
	Sorbitan trioleate	0.20	75
	Polydimethylsiloxane (1000 cstks)	0.01	
	Ferric acetylacetonate	0.10	
	Trioctyl phosphate	4.05	
	Polypropylene glycol 2025	11.65	
	Glyceryl monoricinoleate	2.14	80
	2,4-Tolylene diisocyanate	2.40	
	Polyvinyl chloride resin (GEON 428)	3.00	
	Nitroguanidine	15.00	
		100.00	85

## EXAMPLE VII

	<u>INGREDIENT</u>	<u>WEIGHT PERCENT</u>
25	Ammonium perchlorate – 10 to 48 mesh	53.20
	Ammonium perchlorate – fine grind	7.80
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25
	Calcium oxalate	2.00
30	Lecithin	0.10
	Priminox 10	0.10
	Sorbitan trioleate	0.20
	Polydimethylsiloxane (1000 cstks)	0.01
	Ferric acetylacetonate	0.10
35	Trioctyl phosphate	4.05
	Polypropylene glycol 2025	11.65
	Glyceryl monoricinoleate	2.14
	2,4-Tolylene diisocyanate	2.40
	Polyvinyl chloride resin (GEON 428)	
40	(registered Trade Mark)	1.00
	Nitroguanidine	15.00
		100.00

## EXAMPLE X

	<u>INGREDIENT</u>	<u>WEIGHT PERCENT</u>	
	Ammonium perchlorate*	59.00	90
	Nitroguanidine	15.00	
	Polyvinyl chloride resin (GEON 428)	3.00	
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.50	
	Ferric acetylacetonate	0.10	
	Lecithin	0.10	95
	Priminox 10	0.10	
	Sorbitan trioleate	0.20	
	Polydimethylsiloxane (1000 cstks)	0.01	
	Trioctyl phosphate	4.40	
	Polypropylene glycol 2025 (PPG)	12.64	100
	Glyceryl monoricinoleate (GMRO)	2.33	
	2,4-Tolylene diisocyanate (TDI)	2.62	
		100.00	
	Equivalent percent ratio of monomers PPG/GMRO/TDI of 50/50/110 *87.2:12.8 Ratio of 10 to 48 mesh to fine grind material.		105
			110

## EXAMPLE VIII

	<u>INGREDIENT</u>	<u>WEIGHT PERCENT</u>	
45	Ammonium perchlorate – 10 to 48 mesh	53.20	
	Ammonium perchlorate – fine grind	7.80	
50	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	115
	Calcium oxalate	1.00	
	Lecithin	0.10	
	Priminox 10	0.10	
	Sorbitan trioleate	0.20	
55	Polydimethylsiloxane (1000 cstks)	0.01	120
	Ferric acetylacetonate	0.10	
	Trioctyl phosphate	4.05	
	Polypropylene glycol 2025	11.65	
	Glyceryl monoricinoleate	2.14	
60	2,4-Tolylene diisocyanate	2.40	125
	Polyvinyl chloride resin (GEON 428)	2.00	
	Nitroguanidine	15.00	
		100.00	
65			130

## EXAMPLE XI

	INGREDIENT	WEIGHT PERCENT
5	Ammonium perchlorate*	60.00
	Nitroguanidine	15.00
	Polyvinyl chloride resin (GEON 428)	3.00
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.50
	Ferric acetylacetonate	0.10
10	Lecithin	0.10
	Sorbitan trioleate	0.20
	Priminox 10	0.10
	Polydimethylsiloxane (1000 cstks)	0.01
	Trioctyl phosphate	4.198
15	Polyurethane binder**	16.792
		100.00

\*87.2:12.8 Ratio of 10 to 48 mesh to fine grind material.

20 \*\*Binder composition:  
Equivalent percent ratio of  
monomers PPG/GMRO/TDI of  
50/50/110.

## EXAMPLE XII

	INGREDIENT	WEIGHT PERCENT
	Ammonium perchlorate - 10 to 48 mesh	29.25
	Ammonium perchlorate - fine grind	15.25
30	Ammonium picrate	24.00
	Nitroguanidine	7.50
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25
	Calcium oxalate	2.00
35	Polypropylene glycol 2025	12.40
	Trioctyl phosphate	4.24
	Glyceryl monoricinoleate	2.29
	Lecithin	0.08
	G-2684	0.06
	Polydimethylsiloxane (1000 cstks)	0.01
40	Ferric acetylacetonate	0.10
	2,4-Tolylene diisocyanate	2.57
		100.00

## EXAMPLE XIII

	INGREDIENT	WEIGHT PERCENT
	Ammonium perchlorate - 10 to 48 mesh	30.25
	Ammonium perchlorate - fine grind	15.25
50	Ammonium picrate	24.00
	Nitroguanidine	7.50
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25
	Calcium oxalate	2.00
55	Polypropylene glycol 2025	11.71
	Trioctyl phosphate	4.08
	Glyceryl monoricinoleate	2.16
	Lecithin	0.20
	G-2684	0.06
	Polydimethylsiloxane (1000 cstks)	0.01
60	Ferric acetylacetonate	0.10
	2,4-Tolylene diisocyanate	02.43
		100.00

## EXAMPLE XIV

	INGREDIENT	WEIGHT PERCENT	
	Ammonium perchlorate - 10 to 48 mesh	48.00	70
	Nitroguanidine	15.00	
	Aluminum powder	10.00	
	Calcium oxalate	2.00	
	Lithium carbonate	1.00	
	Oxamide	1.00	75
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	
	Ferric acetylacetonate	0.10	
	Sorbitan trioleate	0.20	
	Lecithin	0.10	
	Priminox 10	0.10	80
	Polydimethylsiloxane (1000 cstks)	0.01	
	Trioctyl phosphate	4.45	
	Polypropylene glycol 2025	12.80	
	Glyceryl monoricinoleate	2.35	
	2,4-Tolylene diisocyanate	2.64	85
		100.00	

## EXAMPLE XV

	INGREDIENT	WEIGHT PERCENT	
	Ammonium perchlorate - 10 to 48 mesh	53.00	90
	Nitroguanidine	15.00	
	Aluminum powder	5.00	
	Calcium oxalate	2.00	95
	Lithium carbonate	1.00	
	Oxamide	1.00	
	N,N'-diphenyl- <i>p</i> -phenylenediamine	0.25	
	Ferric acetylacetonate	0.10	
	Sorbitan trioleate	0.20	100
	Lecithin	0.10	
	Priminox 10	0.10	
	Polydimethylsiloxane (1000 cstks)	0.01	
	Trioctyl phosphate	4.45	
	Polypropylene glycol 2025	12.80	105
	Glyceryl monoricinoleate	2.35	
	2,4-Tolylene diisocyanate	2.64	
		100.00	

It has been pointed out above that sustainer propellants must have relatively low burning rates by comparison with booster propellants. Ideally, there should be about a tenfold difference in burning rate between these two propellants with the burning rate level of the former preferably being about 0.05 in/sec at 60°F and 230 psia. Theoretical calculations have established the optimum range of burning rates for our sustainer propellants to be from about 0.045 to about 0.10 in/sec at 60°F and 230 psia. We have determined by means of numerous tests familiar to those skilled in the propellant art, including many firing tests, that all of the formulations set forth in the above examples yield sustainer propellants having ballistic and physical properties excellently suited to the purpose. Illustrative of the superior quality of our exemplified propellants for sustainer utility is the fact that their burning rates were found to

fall well within the acceptable range set forth above and for the most part within the range from about 0.05 to about 0.07 in/sec at 60°F and 230 psia of pressure.

5 WHAT WE CLAIM IS:-

1. A solid propellant composition comprising a cured intimate mixture of ammonium perchlorate of particle size such as to pass a 10-mesh Tyler standard screen and be retained on a 48-mesh Tyler standard screen; a cross-linked resin binder which comprises the reaction product of a compound having, as its sole reacting groups, not less than two active hydrogen groups capable of polymerizing with an isocyanate of isothiocyanate, and compound having as its sole reacting groups, not less than two groups capable of undergoing a urethane-type reaction with hydroxy or thiol groups; and a fuel which is nitroguanidine, ammonium picrate, cyclonite, pentaerythritoltetranitrate, mannitolhexanitrate, nitrocellulose, or mixtures thereof.

2. The solid propellant composition of Claim 1 containing in addition, a burning rate depressant material.

3. The solid propellant composition of Claim 2 wherein there is present a stoichiometric excess of the compound having, as its sole reacting groups, not less than two groups capable of undergoing a urethane-type reaction with hydroxy groups, the stoichiometric excess being calculated as an excess over all active hydrogen groups capable of polymerizing with an isocyanate initially present.

4. The solid propellant composition of Claim 3 wherein the stoichiometric excess of reactant material containing groups capable of undergoing a urethane-type reaction with hydroxy groups over the reactant material containing active hydrogen groups capable of polymerizing with an isocyanate corresponds to a proportion of from 100 to 115 equivalents of the former for every 100 equivalents of the latter.

5. The solid propellant composition of Claim 2 wherein the compound having two active hydrogen groups capable of polymerizing with an isocyanate is selected from the class consisting of:

- a. alkane diols having a chain length of from 2 to 20 carbon atoms, inclusive;
- b. alkane dithiols having a chain length of from 2 to 20 carbon atoms;
- c. alkene diols;
- d. alkene dithiols;
- e. cycloalkylene diols;
- f. cycloalkylene dithiols;
- g. aromatic diols;
- h. aromatic dithiols;
- i. aliphatic-aromatic diols;
- j. aliphatic-aromatic dithiols;
- k. diols containing hetero atoms;
- l. dithiols containing hetero atoms;

m. dihydroxy polyesters having a molecular weight from 1000 to 2500;

n. polyalkylene ether glycols having a molecular weight from 400 to 10,000;

o. polysulfides with glycol end groups; and mixtures thereof;

and the compound having not less than two groups capable of undergoing a urethane-type reaction with hydroxy or thiol groups is selected from the class consisting of:

- (1) alkane diisocyanates;
- (2) alkane diisothiocyanates;
- (3) alkene diisocyanates;
- (4) alkene diisothiocyanates;
- (5) alkylidene diisocyanates;
- (6) alkylidene diisothiocyanates;
- (7) cycloalkylene diisocyanates;
- (8) cycloalkylene diisothiocyanates;
- (9) cycloalkylidene diisocyanates;
- (10) cycloalkylidene diisothiocyanates;
- (11) aromatic diisocyanates;
- (12) aromatic diisothiocyanates;
- (13) aliphatic-aromatic diisocyanates;
- (14) aliphatic-aromatic diisothiocyanates;
- (15) diisocyanates containing hetero atoms;
- (16) diisothiocyanates containing hetero atoms; and mixtures thereof;

and, in addition, a cross-linking agent compound having, as its sole reacting groups, not less than three groups polymerizable with a radical selected from the groups consisting of hydroxy, thiol, isocyanate, and isothiocyanate groups, and said fuel is selected from the class consisting of nitroguanidine, ammonium picrate, and mixtures thereof.

6. The solid propellant composition of Claim 5, in which the burning rate depressant material is selected from the group consisting of polyvinyl chloride resins, oxamide, calcium oxalate, calcium carbonate, calcium fluoride, calcium phosphate, nickel fluoride, nickel carbonate, nickel phosphate, zirconium silicate, lithium carbonate, diammonium phosphate, magnesium phosphate, sodium tetraborate, calcium metaborate, magnesium metaborate, ammonium phosphomolybdate, the triethanolamine complex of ammonium silicomolybdate, and mixtures thereof.

7. The solid propellant composition of Claim 5, wherein the resin binder comprises the reaction product of a stoichiometric excess of the isocyanate compound, the stoichiometric excess being calculated as an excess over the combined equivalents of the compound containing two hydrogen groups capable of polymerizing with an isocyanate or isothiocyanate and the cross-linking agent.

8. The solid propellant composition of Claim 7, wherein the resin binder comprises the reaction product of from 100 to 115 equivalents of isocyanate compound for every 100 equivalents of the compound having two active hydrogen groups capable of

polymerizing with an isocyanate or isothiocyanate plus the cross-linking agent.

9. The solid propellant composition of Claim 3, wherein the resin binder is present in an amount between 5 and 55 percent by weight; the ammonium perchlorate is present in an amount between 50 and 80 percent by weight; and the fuel is present in an amount between 5 and 40 percent by weight; all percentages being given on a total propellant weight basis.

10. A solid propellant composition comprising a cured intimate mixture of ammonium perchlorate of particle size such as to pass a 10-mesh Tyler standard screen and be retained on a 48-mesh Tyler standard screen; a resin binder which comprises the reaction product of an aromatic diisocyanate, a polyether having a molecular weight between 400 and 10,000, and a trihydroxy cross-linker compound; nitroguanidine; and a burning rate depressant material; the ammonium perchlorate being present in an amount between 50 and 80 percent by weight, the resin binder being present in an amount between 15 and 30 percent by weight, and the nitroguanidine being present in an amount between 5 and 25 percent by weight; all percentages being given on a total propellant weight basis.

11. The solid propellant composition of Claim 10, wherein the aromatic diisocyanate is present in stoichiometric excess over the amounts of polyether and trihydroxy compounds initially present.

12. The solid propellant composition of Claim 11, wherein the trihydroxy cross-linker compound is glyceryl monoricinoleate and in addition there is present trioctyl phosphate.

13. The solid propellant composition of Claim 12, wherein the aromatic diisocyanate is 2,4-tolylene diisocyanate and the polyether is polypropylene glycol having a molecular weight of from 2000 to 3000.

14. The solid propellant composition of Claim 12, wherein the burning rate depressant material is a low molecular weight, low fusion temperature, polyvinyl chloride resin.

15. The solid propellant composition of Claim 12, wherein the burning rate depressant material is calcium oxalate.

16. The solid propellant composition of Claim 12, wherein the burning rate depressant material consists of calcium oxalate and lithium carbonate.

17. The method of preparing a solid propellant composition which comprises intimately dispersing ammonium perchlorate of particle size as to pass a 10-mesh Tyler standard screen and be retained by a 48-mesh Tyler standard screen; a fuel which is nitroguanidine, ammonium picrate, cyclonite, pentaerythritoltetranitrate, mannitolhexanitrate, nitrocellulose or mixtures thereof; and a burning rate depressant

material in a cross-linked resin binder mixture comprising a compound having, as its sole reacting groups, not less than two active hydrogen groups capable of polymerizing with an isocyanate or isothiocyanate and a compound having, as its sole reacting groups, not less than two groups capable of undergoing a urethane-type reaction with hydroxy or thiol groups; and curing the mixture.

18. The method of Claim 17, wherein the fuel is selected from the group consisting of nitroguanidine, ammonium picrate, and mixtures thereof and the compound having two active hydrogen groups capable of reacting with an isocyanate or isothiocyanate is selected from the class consisting of dihydroxy polyesters having a molecular weight from 1000 to 2500, and polyalkylene ether glycols having a molecular weight from 400 to 10,000, and mixtures thereof; and the compound having, as its sole reacting groups, not less than two groups capable of undergoing a urethane-type reaction with hydroxy or thiol groups is selected from the class consisting of alkane diisocyanates, and aromatic diisocyanates, and mixtures thereof.

19. The method of Claim 18, wherein the resin binder is employed in an amount between 5 and 55 percent by weight; the ammonium perchlorate is employed in an amount between 50 and 80 percent by weight, and the fuel is employed in an amount between 5 and 40 percent by weight; all percentages being given on a total propellant weight basis.

20. The method of Claim 19, wherein trioctyl phosphate is added to the binder before curing the mixture.

21. The method of Claim 20, wherein the compound having as its sole reacting groups, not less than two groups capable of undergoing a urethane-type reaction with hydroxy or thiol groups is employed in a stoichiometric excess over the combined amounts of the compound having not less than two active groups capable of polymerizing with an isocyanate or isothiocyanate and the cross-linking agent.

22. The method of preparing a solid propellant composition which comprises intimately dispersing ammonium perchlorate of particle size such as to pass a 10-mesh Tyler standard screen and be retained on a 48-mesh Tyler standard screen; nitroguanidine; a burning rate depressant material; and trioctyl phosphate in a binder mixture comprising 2,4-tolylene diisocyanate, polypropylene glycol having a molecular weight of from 2000 to 3000, and glyceryl monoricinoleate, and curing the mixture; the ammonium perchlorate being present in an amount between 50 and 80 percent by weight of the propellant composition, the nitroguanidine being present in an amount between 5 and 25 percent by weight of the propellant composition, the resin binder being present in an amount

5 between 15 and 30 percent by weight of the  
propellant composition, and the 2,4-tolylene  
diisocyanate being employed in a proportion  
of from 100 to 115 equivalents thereof per  
every 100 equivalents of the combined  
amounts of polypropylene glycol and glyceryl  
monoricinoleate employed.

FRANK B. DEHN  
Chartered Patent Agents  
Imperial House,  
15-19 Kingsway,  
London, W.C.2.

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